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THE UNUSUAL EQUILIBRIUM BETWEEN 1,4- AND 1,6-Di-  
tert-butylcyclooctatetraenes

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and Robert Q. Kluttz

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The Unusual Equilibrium Between 1,4- and  
1,6-Di-tert-butylcyclooctatetraenes

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The Unusual Equilibrium Between 1,4- and  
1,6-Di-tert-butylcyclooctatetraenes

Sir:

We have recently had occasion to prepare 1,4-di-tert-butylcyclooctatetraene as a potentially interesting ligand for uranium.<sup>1</sup> Indeed, the corresponding uranocene did show a rotational barrier about the molecular axis that could be measured by dynamic nmr techniques.<sup>2</sup> The hydrocarbon itself, however, shows some unusual features as regards double-bond isomerism. The hydrocarbon as prepared by oxidation of the corresponding dianion with iodine consists of an equilibrium mixture of the two double bond isomers, 1,6-di-tert-butylcyclooctatetraene, 1, and the 1,4- isomer, 2, as clearly evident in the 250 MHz spectrum. The olefinic region of 2 consists of a singlet (H 2, 3) at  $\delta$  6.05 and two broadened singlets (H 5, 6, 7, 8) at  $\delta$  5.78 and  $\delta$  5.63 while that of 1 consists of a singlet (H 7, 8) at  $\delta$  5.66 and a broadened AB quartet (H 2, 3, 4, 5) centered at  $\delta$  5.89 and  $\delta$  6.03,  $J = 10.4$  Hz. This pattern is consistent with a very small coupling between H2 and H3 of 1 which are nearly orthogonal and a 10 Hz coupling between the cis olefinic H5 and H6 of 2.

Integration gives a 6:4 ratio of 1:2 at 25°C; that is, the 1,6- isomer in which both tert-butyl groups extend from the same side of the tub COT is actually more stable despite the steric interactions between such tert-butyl groups indicated by models.

Measurement of the equilibrium constant,  $K = [2]/[1]$ , by nmr integration at several temperatures gives the results summarized in Table 1. Isomer 1 is more stable by  $\Delta H^\circ = 0.48 \text{ kcal mol}^{-1}$  but a small entropy change of  $\Delta S^\circ = 0.92 \text{ e.u.}$  favors isomer 2. Rotational entropy (symmetry number) and entropy of mixing (2 exists as enantiomer pairs) contributions to the equilibrium cancel; hence, the experimental  $\Delta S^\circ$  change indicates slightly greater freedom of motion for 2.

Why is 1, the apparently more congested isomer, also the more stable? The only reasonable explanation is that the tert-butyl groups in 1 are actually positioned just at the edge of steric repulsion and that intramolecular Van der Waals attraction dominates. Van der Waals forces are certainly important in chemistry but have rarely been implicated as a significant intramolecular effect in nonmacromolecular organic compounds.<sup>3</sup>

Treatment of the mixture of isomers with excess hot alcoholic silver nitrate gives a single crystalline adduct, m.p.  $151^\circ$ , having a satisfactory analysis.<sup>4</sup> The 250 MHz nmr is simple;  $\delta$  ( $\text{CDCl}_3$ ) 6.31 (s, 2H), 5.99 (br s, 2H), 5.72 (br s, 2H), 1.10 (s, 18H), and is consistent only with the  $\text{AgNO}_3$  complex of 1. In 2 both faces of the tub COT are blocked by the t-Bu groups and adduct formation is not expected. Such an adduct would be expected to show 6 different olefin and 2 different t-Bu signals.

A  $\text{CDCl}_3$  solution of the adduct in an nmr tube was quenched with aqueous  $\text{NH}_3$  and produced signals associated with 1. The nmr spectrum changed gradually to that of the equilibrium mixture of

1 and 2. The reaction followed first order kinetics and the kinetic results at several temperatures are summarized in Table 1. The activation energy is typical of other double bond isomerizations of substituted COTs<sup>5</sup> but the magnitude of the entropy of activation,  $\Delta S^\ddagger = -26.3$  e.u., is unusually high for a unimolecular process. Even the isomerizations of 1,2,3-trimethyl ( $\Delta S^\ddagger = -12$  e.u.) and 1,2,3,4-tetramethylcyclooctatetraenes ( $\Delta S^\ddagger = -13.3$  e.u.) as reported by Paquette, et al,<sup>6</sup> and in which vicinal buttressing effects dominate, have lower entropy demands. Evidently, in the planar [8]annulene transition state the relatively large internal angle of the octagon ( $135^\circ$ ) results in sufficient interaction between tert-butyl and adjacent ring hydrogens that the tert-butyl motions are severely encumbered.

These results prompt additional questions concerning disubstituted cyclooctatetraenes which are currently under study in our laboratory.

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1. Miller, M. J., Lyttle, M. R., and Streitwieser, A., Jr., J. Org. Chem., submitted.
2. Luke, W. D., and Streitwieser, A., Jr., J. Am. Chem. Soc., submitted.
3. One example of the incursion of the effect may well be in the unusual conformations preferred by 2,2-dimethyl-4-phenyl-3-pentanol; Kodama, Y., Nishihata, K., Zushi, S., Nishio, M., Uzawa, J., Sakamoto, K., Iwamura, H., Bull. Chem. Soc. Japan, 1979, 52, 2661.
4. Analysis by Analytical Services Laboratory, Univ. Calif., Berkeley: Calcd. for  $C_{16}H_{24} \cdot AgNO_3$ : C, 49.76; H, 6.26; N, 3.63. Found: C, 50.29; H, 6.24; N, 3.69.
5. Anet, F. A. L., J. Am. Chem. Soc., 1962, 84, 671;  
Anet, F. A. L., Bourn, A. J. R., and Lin, Y. S., J. Am. Chem. Soc., 1965, 86, 3576;  
Oth, J. F. M., Pure Appl. Chem., 1971, 25, 573;  
Gwynn, D. E., Whitesides, G. M., and Roberts, J. D., J. Am. Chem. Soc., 1965, 87, 2862.
6. Paquette, L. A., and Gardlik, J. M., J. Am. Chem. Soc., 1980, 102, 5016;  
Paquette, L. A., Gardlik, J. M., Johnson, L. K., and McCullough, K. J., J. Am. Chem. Soc., 1980, 102, 5026.
7. N.S.F. Postdoctoral Fellow, 1980.



Table 1. Forward rates and equilibrium constants for  $\underline{1} \rightleftharpoons \underline{2}$ 

Temp, °C	$10^4 \underline{k}_1, \text{sec}^{-1}$ <sup>a</sup>	$\underline{K} = [\underline{2}]/[\underline{1}]$ <sup>b</sup>
25	2.0	0.702
30	2.6	.714
40	5.7	.728
45	10.2	.739
50		.750

(a).  $\Delta H^\ddagger = 14.7 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -26.3 \text{ e.u.}$

(b).  $\Delta H^\circ = 0.48 \text{ kcal mol}^{-1}$ ,  $\Delta S^\circ = 0.92 \text{ e.u.}$

Abstract. Oxidation of 1,4-di-tert-butylcyclooctatetraene dianion with iodine gives an equilibrium mixture of 1,6-,  $\underline{1}$ , and 1,4-di-tert-butylcyclooctatetraene,  $\underline{2}$ . The equilibrium constant at 25°,  $\underline{K} = [\underline{2}]/[\underline{1}] = 0.702$ ;  $\Delta H^\circ = 0.48 \text{ kcal mol}^{-1}$ ,  $\Delta S^\circ = 0.92 \text{ e.u.}$  The surprisingly greater stability of  $\underline{1}$  is explained by a dominant intramolecular Van der Waals attraction. Treatment with  $\text{AgNO}_3$  gives the complex only of  $\underline{1}$ . Reaction of the  $\text{AgNO}_3$  complex with aq.  $\text{NH}_3$  regenerates  $\underline{1}$  which gradually undergoes double bond isomerism to the equilibrium mixture with the activation parameters,  $\Delta H^\ddagger = 14.7 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -26.3 \text{ e.u.}$

